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PROJECT NAME: Waukegan

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TREATABILITY STUDY WORK PLAN

WAUKEGAN MANUFACTURING GAS AND COKE PLANT
WAUKEGAN, ILLINOIS

JUNE 2000
REF. NO. 15670 (5)
This report is printed on recycled paper.

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1.0 INTRODUCTION

This Treatability Study Work Plan, prepared by Conestoga-Rovers & Associates, is based on the May 23, 2000 "Pilot Project Work Plan, Waukegan Manufactured Gas and Coke Plant, Waukegan Illinois", Newfields, Inc.

The purpose of the treatability study is to evaluate potential treatment technology for groundwater collected at the Site. The treatment technology will address all relevant constituents regulated under State Drinking Water Act, 35, Illinois Administrative Code Part 620 and the Resource Conservation and Recovery Act.

The groundwater treatability studies will consist of two basic parts; pretreatment for arsenic removal and biological treatment for removal of organic constituents, ammonia and thiocyanate. It is expected that during pretreatment partial removal of thiocyanate and phenols will also be achieved.

A minimum 75 gallons of equalized groundwater sample from the Site will be shipped to the CRA Treatability Laboratory in Waterloo, Ontario. The sample will be the subject of initial screening tests to determine the optimum pretreatment conditions. The whole sample will then be treated to remove arsenic using Fenton's reagent (hydrogen peroxide and ferrous sulfate mixture).

The pretreated sample will be the subject of biological treatment using a biomass from a full-scale activated sludge treatment plant that treats coke plant wastewater (expected to be from US Steel-Gary Works) and achieves both biological organic removal and nitrification. The bench scale biological treatment studies will be conducted using two separate treatment trains with sequencing batch reactors (SBR). One system will apply one reactor and the same biomass to remove organic contaminants and ammonia. The other system will consist of two reactors in series; the first reactor dedicated to organics removal and the second to nitrification.

2.0 SAMPLE COLLECTION STORAGE AND HANDLING

One of the most important issues in any treatability study is the collection and preservation of a representative sample of the water to be treated.

To ensure the representativeness of the sample collected at the Site the following procedure will be followed:

i) 75 gallons of water will be collected from the first bulk storage tank when the tank is initially filled during the pilot extraction and re-injection test;

ii) the groundwater sample will be collected from the middle of the tank avoiding any aeration; and

iii) after collection the groundwater will be shipped immediately in headspace free containers to the laboratory.

To ensure the same quality of the groundwater during the studies the following procedures will be applied:

i) containers will be kept at ~ 5°C and well mixed before the treatment;

ii) samples for any studies will be collected in equal amounts from each of the shipping containers; and

iii) before treatment each sample will be analyzed for basic general chemistry parameters [pH, total suspended solids (TSS), turbidity, conductivity, chemical oxygen demand (COD), soluble COD (SCOD), ammonia].

3.0 ARSENIC PRETREATMENT WITH FENTON'S REAGENT

The main purpose of pretreatment of the groundwater is to remove arsenic to mitigate the inhibitory effect of arsenic on biological treatment, particularly on nitrification. Application of Fenton's reagent , a strong oxidant, should also stimulate partial removal of thiocyanate and phenols that are also inhibitory to biological treatment at higher concentrations.

Pretreatment studies will include initial optimization tests and full bench-scale tests.

3.1 INITIAL OPTIMIZATION TESTS

Since efficiency of arsenic and organics treatment using Fenton's reagent strongly depends on the chemistry of the water to be treated it will be necessary to determine the optimum conditions (pH, hydrogen peroxide/ferrous sulfate ratio, reaction time) for the treatment.

The following procedures will be applied:

Test (1):

500 mL groundwater samples will be treated with the same amount of ferrous sulfate and various amounts of hydrogen peroxide. The range of hydrogen peroxide and ferrous concentrations to be used will be calculated based on the COD of the water and concentrations of phenols, thiocyanate and arsenic.

Test (2):

500 mL groundwater samples will be treated with the same amount of hydrogen peroxide and various amounts of ferrous sulfate.

After treatment each sample will be analyzed for TSS, arsenic, total organic carbon (TOC), phenols and thiocyanate. Each test will be conducted in triplicate and the results will be evaluated using statistical methods.

Test (3):

500 mL groundwater samples will be treated with various doses of Fenton's reagent optimized in Tests 1 and 2 at various pH (range 3.5 – 7.0) and various reaction times

(20 minutes – 60 minutes). Treated samples will be analyzed for TSS, arsenic, TOC, phenols and thiocyanate. Each test will be conducted in triplicate and the results will be evaluated using statistical methods. A list of analytical methods used in the studies is presented in Table 1.

3.2 BENCH-SCALE PRETREATMENT

Approximately half of the groundwater volume collected at the Site will be pre-treated in several batches with Fenton's reagent in conditions optimized in Tests 1, 2 and 3. The balance of the raw groundwater will be subsequently pre-treated by the optimized process when it is required to supply on-line influent to the final long-term biological study described in Section 4.0. A small sample, approximately 1 gallon, of raw water will be stored as a reference. A composite of raw samples will be analyzed for pH, TSS, volatile suspended solids (VSS), COD, TOC, dissolved organic carbon (DOC), phenols, arsenic, ammonia, nitrates, cyanide, thiocyanate as well as for acid and base/neutral organic constituents using analytical methods presented in Table 1.

During bench scale pretreatment, the settling time of precipitated solids and the necessity of using organic flocculent will be also evaluated. Supernatant from the treatment will be collected for biological studies and analyzed for pH, TSS, VSS, COD, TOC, DOC, phenols, arsenic, ammonia, nitrates, cyanide, and thiocyanate. These samples will also be analyzed for acid and base/neutral organic constituents. A list of analytical methods used in the studies is presented in Table 1. A list of sampling and analyses that will be conducted during pretreatment is presented in Table 2.

Separated solids will be dewatered using membrane filters. Filter cake will be the subject of TCLP leachability tests for arsenic, phenols, benzene and thiocyanate. The solids generation rate will be estimated from the TSS results.

4.0 BIOLOGICAL TREATMENT

Biological studies will consist of the following activities:

i) acclimatization (3 to 5 days);

ii) initial tests for one solid retention time (SRT approximately 15 to 20 days); and

iii) final long-term test (approximately 4 to 5 weeks).

4.1 ACCLIMATIZATION

The purpose of acclimatization is to prepare the biomass to treat the target water. Since each water stream to be treated has a specific water quality, microorganisms have to modify their metabolic processes to use particular components of the groundwater as a source of food and energy.

The biomass used in the studies will be collected from returned activated sludge at a wastewater treatment plant in the US Steel-Gary Works, Gary Indiana. This plant is reported to treat coke plant wastewater and achieves biological removal of organics and ammonia. The biomass will be shipped to the CRA Treatability Laboratory immediately after collection in three 5-gallon plastic containers. The containers will have enough headspace to maintain aerobic conditions during shipment. The dissolved oxygen concentration will be measured several times prior to shipping the containers. If the concentration of oxygen in the biomass will not be sufficient (<2 mg O_2/L) and or rapidly decreases then hydrogen peroxide will be added prior to shipping.

The following acclimatization procedure will be followed in the laboratory.

Initially, approximately 1 L of the biomass will be placed in each biological reactor (SBR-1, SBR-2 and SBR-3) and aerated for 5 hours. Samples of the biomass will be examined under the microscope every hour to ensure its good quality.

All reactors will then be fed with a small volume (approximately 100 mL) of pretreated wastewater. In addition reactor SBR-3 will be fed with 20 mg/L ammonium chloride to stimulate growth of nitrifying bacteria. After wastewater addition samples from all reactors will be collected and analyzed for pH, TSS, VSS, phenols, COD, SCOD, ammonia and nitrates. After 1 day of aeration samples will be collected and analyzed for the same parameters. If results of the analyses indicate substantial removal of COD and ammonia more wastewater will be gradually added to reactors SBR-1 and SBR-2,

while reactor SBR-3 will be fed with the mixture of supernatant from reactor SBR-2 and ammonium chloride. Samples of supernatant from all reactors will be collected daily and analyzed for TSS, VSS, COD, SCOD, ammonia and nitrate. Daily samples of the biomass will also be collected and examined under the microscope to assess the vitality and diversity of the microorganisms.

Acclimatization of the biomass will be completed when substantial removal (>60%) of SCOD and ammonia will occur despite increasing the amount of pretreated groundwater added to the bioreactor. At the same time microscopic examination of the biomass should indicate diversity and vitality of microorganisms.

4.2 INITIAL BIOLOGICAL TESTS

The purpose of initial biological testing is to determine any variation in each system's performance based on the same 6-hour cycles comprised of the following periods:

- aerated fill - 2 hours;
- aerated react - 2.5 hours;
- settle - 1 hour; and
- draw - 0.5 hour.

Tests will be conducted in 1-gallon tanks equipped with a mechanical mixer and aerators. Influent to the reactors and effluent from the reactors will be pumped using peristaltic pumps. To ensure the same duration of treatment cycles in all reactors, peristaltic pumps will be connected to an electrical timer. Activated sludge will be wasted regularly at a rate that allows maintaining a design concentration of the biomass in each reactor.

The following operating parameters will be applied:

	SBR –1	*SBR-2*	*SBR-3*
Hydraulic Retention Time (hours)	24	24	24
Solids Retention Time (days)	6-10	15-20	15-20
Dissolved Oxygen (mg O2/L)	> 2	> 2	> 2
Mixed Liquor Suspended Solids (mg/L)	2000-3000	3000-5000	3000-5000

Reactors SBR-1 and SBR-2 will be fed with pretreated groundwater while reactor SBR-3 will be fed with the effluent from reactor SBR-2.

Samples from the same cycle of each reactor will be collected daily and analyzed for pH, TSS, COD, phenols, cyanide, thiocyanide and ammonia. At the same time the effluent from SBR-1 and SBR-3 will be collected separately during the final 5 days of the test. Both collected effluents will be analyzed for TSS, VSS, COD, TOC, DOC, phenols, arsenic, ammonia, nitrate, cyanide, and thiocyanate. These samples will also be analyzed for organic constituents using GC/MS technique (acid and base/neutral methodology). A list of analytical methods used in the studies is presented in Table 1. A list of sampling and analyses that will be conducted during initial biological tests is presented in Table 3.

Based on the results of the analyses, the variations of parameters during a single cycle as well as the average performance of each treatment train will be determined. These data will also be used for comparison with the results of the final long-term biological treatment.

4.3 LONG –TERM BIOLOGICAL TREATMENT

During the long-term biological treatment the lengths of the various stages of the treatment cycle will be optimized. The impact of aerobic and anoxic stages on system performance will also be investigated. Each treatment system will operate with one variable changed for 5-6 days and samples will be collected daily after each treatment stage.

In order to simulate full-scale conditions both treatment trains will be fed with freshly pretreated groundwater.

The following treatment strategy will be applied:

SBR-1

This reactor is designed to remove all organic substances and ammonia using the same biomass.

Initially the reactor will be filled without aeration but with mixing for 1 hour. The lengths of aerobic react time (2.5 hours) and settle time (1 hour) will be the same as was applied during initial biological tests. Then the impact of various sequences of aerobic

and anoxic periods on effluent quality will be investigated. After the impact of variables has been evaluated the system will run under optimized conditions for a week.

SBR-2 and SBR-3

Reactor SBR-2 is designed to remove most of the organic load using specialized biomass while reactor SBR-3 is designed to remove ammonia and denitrify using a different biomass. At the same time the quality of the effluent from SBR-2 will affect the performance of SBR-3.

Initially the duration and length of treatment stages will be modified in SBR-2 while the set-up for SBR-3 will be kept as in Section 4.2. Then using optimized set up in SBR-2, the impact of variables on SBR- 3 treatment will be investigated. Finally both reactors will run in optimized cycles for approximately 1 week.

Samples of the effluent from SBR-1, SBR-2 and SBR-3 will be collected daily and analyzed for TSS, VSS, COD, TOC, DOC, phenols, arsenic, ammonia, nitrate, cyanide, and thiocyanate. Composite samples after a few days run with the same set-up will also be analyzed for organic constituents using GC/MS techniques (acid and base/neutral methodology) and analytical methods presented in Table 1. A list of sampling and analyses that will be conducted during this phase of the studies is presented in Table 4.

5.0 TREATMENT ASSESSMENT AND DATA ANALYSIS

Based on treatability studies data the following goals will be accomplished:

i) Determination of treatment efficiency of each element of investigated systems based on removal of arsenic, organic constituents, thiocyanate, cyanide and ammonia; mass balance of each constituent during pretreatment and biological treatment will provide sufficient data to calculate the removal efficiency and estimate the cost for their removal in the full-scale design;

ii) Identification of variables affecting the efficiency of treatment for each parameter of concern; statistical analyses of treatability data will allow determination of a parameter affect on the removal of a particular constituent and operational changes required to respond to potential changes in the quality of the groundwater during full-scale treatment; and

iii) Treatment process design; treatability data will allow the calculation of reaction rate coefficients for each parameter of interest. These coefficients can then be used to design the full-scale treatment process and estimate the sizes of specific treatment units and sludge generation rates; and

iv) Reinjection effect; results will be evaluated to asses potential effects on the reinjection equipment and in the aquifer.

6.0 TREATABILITY STUDY SCHEDULE

After arrival of the groundwater and activated sludge samples at the CRA Treatability Laboratory the following activities will be implemented:

Week 1

i) Optimization of Fenton's reagent treatment as described in Section 3.1

ii) Acclimatization of the activated sludge in shipping containers to the water pretreated during optimization of Fenton's reagent treatment; and

iii) Set-up of biological treatment systems.

Week 2

i) Bench-scale pre-treatment of the groundwater using procedure described in Section 3.2; and

ii) Acclimatization of the activated sludge in reactors SBR-1, SBR-2 and SBR-3, according to the procedure described in Section 4.1.

Weeks 3 – 4

i) Start-up of two initial biological treatment trains using acclimatized activated sludge and the water pre-treated with Fenton's reagent;

ii) Daily monitoring of the treatment system according to the procedure described in Section 4.2; and

iii) TCLP test with solids generated during bench-scale pre-treatment of the groundwater with Fenton's reagent.

Weeks 5 – 9

i) Long term biological treatment according to the procedure described in Section 4.3.

Weeks 10 - 11

Data compilation and evaluation of treatment as described in Section 5.

7.0 REPORTING

A report generated from the treatability study will consist of the following elements:

- Detailed testing procedures including sampling and analyses;
- Description of equipment used during the study;
- Summary of data from pre-treatment including tables and graphs demonstrating the effect of Fenton's reagent composition and concentration on the removal of arsenic, COD, thiocyanate and phenols;
- Analyses of data from biological treatment of the water that will identify the operational parameters affecting removal of organic substances, thiocyanate and ammonia;
- Summary of data from the whole treatment system that will allow optimization of the full-scale treatment plant; and
- Evaluation of the potential impact of re-injection of the effluent from the treatment plant into the aquifer on the groundwater quality.

TABLES

TABLE 1

LIST OF ANALYTICAL METHODS
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Parameter	*Matrix*	*Method*
Total Phenolics	Water	EPA 420.2
Arsenic	Water	SW-846 6010B
Ammonia	Water	EPA 350.1
VOCs	Water	SW-846 8260B
SVOCs	Water	SW-846 8270C
Nitrate	Water	EPA 353.4
COD	Water	EPA 410.4
TOC	Water	SM 5310B
Cyanide	Water	EPA 335.4
Thiocyanite	Water	SM 4500-CN M
TSS	Water	EPA 160.2
VSS	Water	EPA 160.3
pH	Water	EPA 150.1
Turbidity	Water	SM 2130B
Conductivity	Water	SM 2510B

TABLE 2

SAMPLING AND ANALYSES DURING PRETREATMENT
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Sample	*Sampling*	*Analyses*												
		pH	*TSS*	*VSS*	*COD*	*TOC*	*DOC*	*Phenols*	*Arsenic*	*Cyanide*	*Thiocyanite*	*Ammonia*	*GC/MS Acid*	*GC/MS Base/neutral*
Raw Water	Each Batch	X	X		X	X	X	X	X	X	X			
	Composite	X	X	X	X	X	X	X	X	X	X	X	X	X
Petreated Water	Each Batch	X	X		X	X	X	X	X	X	X			
	Composite	X	X	X	X	X	X	X	X	X	X	X	X	X

TABLE 3

SAMPLING AND ANALYSES DURING INITIAL BIOLOGICAL TESTS
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Sample	*Sampling*	*Analyses*													
		pH	*TSS*	*VSS*	*COD*	*TOC*	*DOC*	*Phenols*	*Arsenic*	*Cyanide*	*Thiocyanite*	*Ammonia*	*Nitrate*	*GC/MS Acid*	*GC/MS Base/neutral*
Influent	Daily	X	X	X	X	X	X	X	X	X	X	X	X	X	X
SBR 1 - 3	Before Fill	X	X	X	X	X	X	X	X	X	X	X	X		
	Fill	X	X	X	X	X	X	X	X	X	X	X	X		
	Draw	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Effluent	Daily	X	X	X	X	X	X	X	X	X	X	X	X	X	X

TABLE 4

SAMPLING AND ANALYSES DURING LONG TERM BIOLOGICAL TESTS
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Sample	*Sampling*	*Analyses*													
		pH	*TSS*	*VSS*	*COD*	*TOC*	*DOC*	*Phenols*	*Arsenic*	*Cyanide*	*Thiocyanite*	*Ammonia*	*Nitrate*	*GC/MS Acid*	*GC/MS Base/neutral*
Influent	Daily	X	X	X	X	X	X	X	X	X	X	X	X	X	X
SBR 1 & 2	Before Fill	X	X	X	X	X	X	X	X	X	X	X	X		
	Draw	X	X	X	X	X	X	X	X	X	X	X	X	X	X
SBR 3	Draw	X	X	X			X	X				X	X		